CONVERSION OF MANURE TO OIL BY HYDROTREATING

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INTRODUCTION

In an effort to utilize a significant potential energy source and at the same time reduce pollution, the Bureau of Mines has been experimentally converting organic wastes to oil. The original process (1,2) uses carbon monoxide and water to treat the organic material at temperatures of 350°-400°C and pressures near 4000 psi. Even though this reaction proceeds well and produces a good yield of oil, there are some technical problems that have to be resolved before the process would be economical. The major problems include the high operating pressure, the large amounts of energy necessary for heating the water reactant, and the purification of the process water containing organic solubles.

In our previous study (3) on bovine manure conversion, we reported that significant improvements in reducing operating pressure and energy requirement for heating were achieved by replacing large percentages of water with a suitable high boiling vehicle. It was also shown that synthesis gas can be used in place of carbon monoxide to convert manure to oil in reasonably good yield. The present work deals with further attempts to use manure-derived oil as a recycle vehicle in place of water. We have found that manure oil is an unsuitable vehicle, giving poor conversion and oil yield in the absence of a suitable catalyst. However, bovine manure, like coal, can be hydrogenated and liquefied at elevated temperatures and pressures in the presence of a vehicle and a cobalt molybdate catalyst. This process may be uneconomical because it requires fairly large amounts of expensive hydrogen in the reaction. A promising method for hydrotreating organic wastes using synthesis gas and a combination of cobalt molybdate-sodium carbonate catalyst is presented in this report. The proposed process requires no process water and results in the effective hydrogenation and deoxygenation of organic wastes without a significant consumption of hydrogen.

EXPERIMENTAL

The conversion of manure to oil was studied in a 500-ml magnetically-stirred, stainless steel autoclave. Bovine manure from Beltsville, Maryland, was used. Chemical analyses of two samples used are given in Table 1. A high boiling alkylnaphthalene-based oil (boiling above 235°C) and manure-derived oils were used as vehicles. A manure oil produced from the reaction of manure with CO and H_2O at 380° and 4500 psi was used as the starting vehicle. In several series of experiments using different gas reactants or catalytic conditions, each succeeding run within a series utilized the oil product recovered from the preceding run as the vehicle. The catalyst was a commercial cobalt molybdate supported on silica alumina used either in the presence or absence of sodium carbonate.

TABLE 1. Analyses of bovine manure (as used), percent

Sample	C	H	N	S	O (by diff.)	Ash	Moisture
1	44.2	6.2	2.5	0.35	39.9	6.9	3.8
2	42.5	5.7	2.3	0.35	34.7	14.5	4.2

For most of these experiments, hydrogen and synthesis gas (approximately equal parts of hydrogen and carbon monoxide) were used as gas reactants at initial pressures of 1000 to 1500 psi. Operating pressures ranged from 2000 to 3000 psi at reaction temperatures of 330° to 425°C, and the reaction was maintained for 15 to 60 minutes at the reaction temperature. After the experiment, rapid internal cooling of autoclave to ambient temperature was achieved. Total products were centrifuged at ambient temperature to obtain centrifuged liquid oils. Centrifuge cakes containing residue and water were extracted by benzene. The water was removed by azeotropic distillation and the remaining oil was recovered by removing the benzene with a rotary vacuum evaporator. Gaseous products were analyzed by mass spectrometry. Data on conversion, oil yield, hydrogen consumption, and carbon dioxide formation, etc., are given as weight percent based on moisture- and ash-free manure.

RESULTS AND DISCUSSION

Effects of Catalyst and Vehicle

The conversion of bovine manure to oil by reaction with synthesis gas is greatly influenced by the presence or absence of catalyst and vehicle. Initial experiments showed that bovine manure could be converted to oil by a mild hydrotreating with hydrogen or synthesis gas in the presence of alkylnaphthalene oil as vehicle. When a manure oil was used as vehicle, however, manure conversion and oil yield were poor, and the oil product became more viscous after each successive run. The use of sodium carbonate as catalyst (1) did not improve the oil quality. After being hydrotreated in the presence of a CoMo catalyst, manure oil became a good vehicle, and successive runs using the manure oil product as vehicle in the presence of CoMo catalyst gave good results. The fluidity of vehicle oil could be maintained throughout many successive runs, suggesting the feasibility of using manure oil product as a recycling vehicle. Analyses of vehicles are given in Table 2. Note that properties of manure oil are improved after hydrotreating with either hydrogen or synthesis gas in the presence of a CoMo catalyst. The oxygen content and oil viscosity are reduced. Effects of vehicle and catalyst on the conversion of manure to oil by hydrotreating with synthesis gas are shown in Table 3. At temperatures of 380° and 425°C and an operating pressure of about 3000 psi, both alkylnaphthalene oil and manure oil used as vehicle gave high conversion and good oil yield when the CoMo catalyst was present.

TABLE 2. Analyses of vehicles, percent

	C	H	N	S	O (by diff.)	Kinematic viscosity, centistoke at 60°C
Alkylnaphthalene oil	90.6	8.7	0.06	0.37	0.3	1.7
Manure oil[a]	80.7	9.6	4.0	0.20	5.5	550
Treated manure oil[b]	80.9	10.3	4.5	0.21	4.1	120
Treated manure oil[c]	83.8	10.2	4.6	0.11	1.3	17

[a] Prepared by reaction of manure with CO and H_2O at 380°C and 4500 psi.
[b] Manure oil was hydrogenated with H_2 at 380°C and 2200 psi in the presence of a CoMo catalyst.
[c] Manure oil was hydrotreated with synthesis gas at 425°C and 2600 psi in the presence of a CoMo catalyst.

TABLE 3. Effects of vehicle and catalyst on conversion of manure

(vehicle:manure = 2.3:1, 1500 psi initial synthesis gas pressure)

Vehicle	Alkylnaphthalene oil				Manure oil	
Temperature, °C	380	380	425	425	380	425
Catalyst[a]	-	CoMo	-	CoMo	CoMo	CoMo
Operating pressure, psi	3200	3000	3200	3100	3000	3000
Time, min.	30	30	15	15	30	15
Conversion, percent[b]	86	92	88	95	93	93
Oil yield, percent[b]	34	47	35	45	45	40

[a] Two parts catalyst per 100 parts feed of manure plus vehicle.
[b] Weight percent of maf manure.

Effects of Gas Reactants

To determine the effects of various gas reactants on the conversion of manure, hydrogen, carbon monoxide, and synthesis gas were compared. Vehicle oils for different runs were conditioned by pretreating with the different gases at desired experimental conditions. At an initial pressure of 1500 psi, operating pressures at 380°C reaction temperature ranged from 2600 to 3500 psi, depending on the extent of hydrogen consumption or hydrogen formation during the reaction. Data are given in Table 4.

Experiments with hydrogen indicate that cobalt molybdate catalyzes the hydrogenation reaction under the operating conditions. The conversion, oil yield, and hydrogen consumption were increased by the use of the catalyst. When carbon monoxide or carbon monoxide and water were used to react with manure, both conversion and oil yield were low, and the oil product behaved poorly as a vehicle. But synthesis gas could be used in place of hydrogen without adverse effects on manure conversion, oil yield, and oil quality. In this comparison, hydrogen consumption decreased from 3.0 to 2.3 percent, water yield decreased from about 23 to 13 percent, but carbon dioxide formation increased considerably. The oxygen content in manure was removed in the form of water and carbon dioxide in both cases.

TABLE 4. Effects of gas reactants on conversion[a]

(manure oil:manure = 2.3:1, 30 minutes at 380°C)

Gas reactant	H_2		CO		H_2 + CO (1:1)	
Catalyst[b]	-	CoMo	-	CoMo	-	CoMo
Initial pressure, psi	1500	1500	1500	1000[c]	1500	1500
Operating pressure, psi	2900	2700	3500	2900	3200	3000
Conversion, percent	78	97	72	84	81	93
Oil yield, percent	23	47	19	34	23	45
H_2 consumption, percent	2.2	3.0	(1.2)[d]	(1.6)[d]	1.4	2.3
CO_2 formation, percent	17	16	78	86	60	42

[a] Data are given in weight percent of maf manure.
[b] Two parts of catalyst per 100 parts feed of manure plus manure oil.
[c] Water (33 parts per 100 parts manure) was also added as the reactant.
[d] Hydrogen formation.

Effects of Reaction Variables

Pressure. The effect of operating pressure on the conversion of manure was studied for both hydrogen and synthesis gas. The reactions were carried out at 380°C for 30 minutes. Starting at the same initial pressures, the hydrogen runs did not reach as high operating pressures as the synthesis gas runs, probably because of the greater hydrogen consumption. As shown in Figure 1, the conversion and the oil yield increase slightly with pressure in the range of 1500 to 3000 psi, but there are very little differences between hydrogen and synthesis gas.

Temperature. Of all the variables investigated, temperature has the most dramatic effect on the properties of the oil product. Experiments were conducted at an initial pressure of 1500 psi but at different operating pressures, ranging from 2600 to 3100 psi, depending on the reaction temperature and gas reactant. The reaction was maintained for different periods at different temperatures: 60 minutes at 330°C, 30 minutes at 380°C, and 15 minutes at 425°C. The results in Table 5 indicate, for both hydrogen and synthesis gas runs, that the hydrogen consumption increased with temperature without improvements in the conversion or oil yield. However, significant improvements in oil product quality were observed with increasing temperature; carbon content increased, oxygen content decreased, and viscosity was reduced. The change in the properties of oil product is accompanied by some decrease in the oil yield, mainly because the oxygen-containing groups are further reduced and the product oil is subjected to cracking. The amount of low molecular weight hydrocarbon gases produced was small but increased with temperature. Again, in comparison with the hydrogen runs, the synthesis gas runs yielded greater amounts of carbon dioxide but smaller amounts of water. In the hydrogen runs, the constant amount of carbon dioxide formed (average 16 percent) is probably all that could be produced from the thermal decomposition of the manure.

TABLE 5. Hydrotreating of manure at various temperatures[a]

(manure oil:manure = 2.3:1, CoMo catalyst, 1500 psi initial pressure)

	H_2			$H_2 + CO$ (1:1)		
Temperature, °C	330	380	425	330	380	425
Operating pressure, psi	2600	2700	2700	3100	3000	3000
Time, minutes	60	30	15	60	30	15
Conversion, percent	95	97	94	94	93	93
Oil yield, percent	49	47	39	47	45	40
CH_4 formation, percent	0.3	0.9	2.7	0.5	1.3	3.5
CO_2 formation, percent	17	16	16	31	42	47
H_2O yield,[b] percent	20	23	25	16	13	10
H_2 consumption, percent	2.3	3.0	4.5	2.0	2.3	2.6
Oil analysis, percent						
C		81.9		77.5	81.5	83.4
H		9.7		9.8	9.9	10.2
N		4.2		4.3	4.4	4.6
S		0.18		0.19	0.10	0.11
O (by diff.)		4.0		8.2	4.1	1.7
Kinematic viscosity of oil at 60°C, centistoke		118		563	129	17

[a] Data are given in weight percent of maf manure.
[b] Excluding moisture content in manure.

Reaction Time. Figure 2 shows the effect of time on the conversion of manure by hydrogen at 380°C. The time required to reach 380°C in the autoclave was about 60 minutes, and the reaction was then maintained at this temperature from 0 to 60 minutes. Nearly 85 percent of conversion occurred before the system reached 380°C, and the conversion approached a limit of about 97 percent after the reaction was in progress at 380°C for 30 minutes. All carbon dioxide was produced before the reaction mixture reached 380°C (before zero time). The progress of the hydrogenation, and probably the upgrading of the oil properties, can be better measured by the hydrogen consumption which increased from 1.4 percent at zero time to 3.6 percent at 60 minutes.

Effect of Sodium Carbonate

Two comparative series of experiments were carried out hydrotreating bovine manure. In the first series, manure was hydrotreated with synthesis gas at an initial pressure of 1000 psi and 380°C reaction temperature for 30 minutes in the presence of a CoMo catalyst and a manure oil vehicle. Various amounts of water (0 to 50 parts per 100 parts of manure) were added in different runs to determine the effect of moisture content of manure. In each succeeding run, the oil product recovered from the preceding run was used as vehicle. In the second series, experiments were carried out in the similar manner except that 2 percent Na_2CO_3 (based on feed of manure plus vehicle) was added in addition to the CoMo catalyst.

Results are shown in Table 6. Operating pressures were higher in Series 2 than in Series 1 at equal water levels. The average oil yield in the presence of Na_2CO_3 increased and the kinematic viscosity of the product decreased. In addition, hydrogen consumption was reduced as shown in Figure 3. Less hydrogen was consumed with increasing moisture content of manure, without any effect on the conversion of manure to oil. Other noticeable effects of the Na_2CO_3 addition were increased carbon dioxide formation and decreased water yield. It is apparent that in the presence of Na_2CO_3, hydrogen consumed is partly replenished by the reaction of carbon monoxide with water during hydrotreating. As a result, effective hydrogenation and deoxygenation of manure are accomplished without significant consumption of hydrogen.

CONCLUSIONS

Bovine manure is hydrogenated and liquefied by hydrogen or synthesis gas (equal amounts of hydrogen and carbon monoxide) at temperatures of 330° to 425°C and operating pressures of 1500 to 3000 psi in the presence of a recycle manure oil and a cobalt molybdate catalyst. With an increase in temperature, oxygen content and viscosity of oil product decrease, but hydrogen consumption increases. Synthesis gas can be used in place of hydrogen to reduce hydrogen consumption without adverse effects. A significant improvement on this process, when using synthesis gas, is achieved by adding sodium carbonate to the reaction mixture; hydrogen consumption is reduced markedly, oil yield improved, and oil viscosity reduced. Manure with moisture contents up to about 35 weight percent was evaluated and found acceptable as feedstocks. The other feature of the process is that it requires no process water, and this eliminates the problem of heating or purifying large amounts of the process water.

REFERENCES

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TABLE 6. Effect of Na_2CO_3 on hydrotreating of bovine manure by synthesis gas

(manure oil:manure:water = 2.3:1:0-0.5, 1000 psi initial pressure, 380°C, 30 minutes)

Series	Catalyst	Operating pressure,[a] psi	Conversion, percent	Oil yield, percent	H_2 consumption, percent	CO_2 formation, percent	Kinematic viscosity,[b] cs at 60°C
1	CoMo	2100-2700	95-98	42-44	1.0-2.1	34-45	138
2	CoMo-Na_2CO_3	2200-3000	95-98	46-48	(0.75)[c]-0.4	67-86	65

[a] Operating pressure increased with the amount of water added.
[b] Kinematic viscosity of the oil product obtained at the end of the series.
[c] Hydrogen formation.

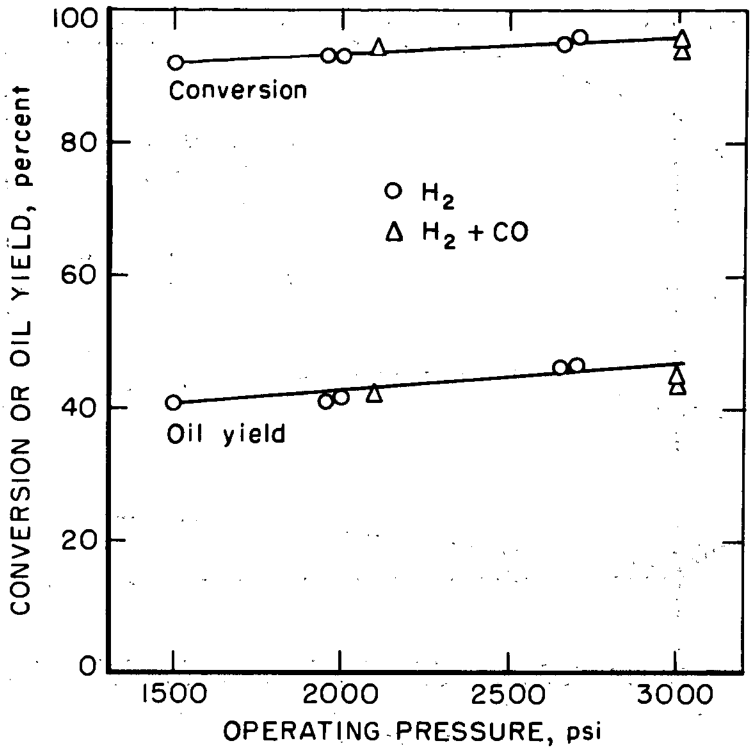

Figure 1 – Effect of operating pressure on conversion of manure at 380° C

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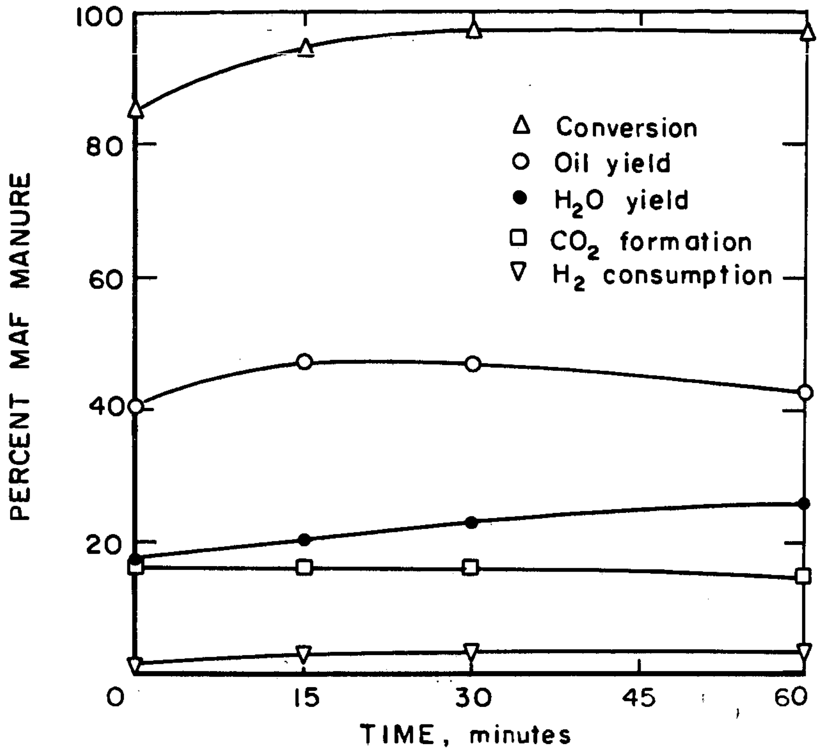

Figure 2– Effect of time on conversion of manure by H_2 at 380°C.

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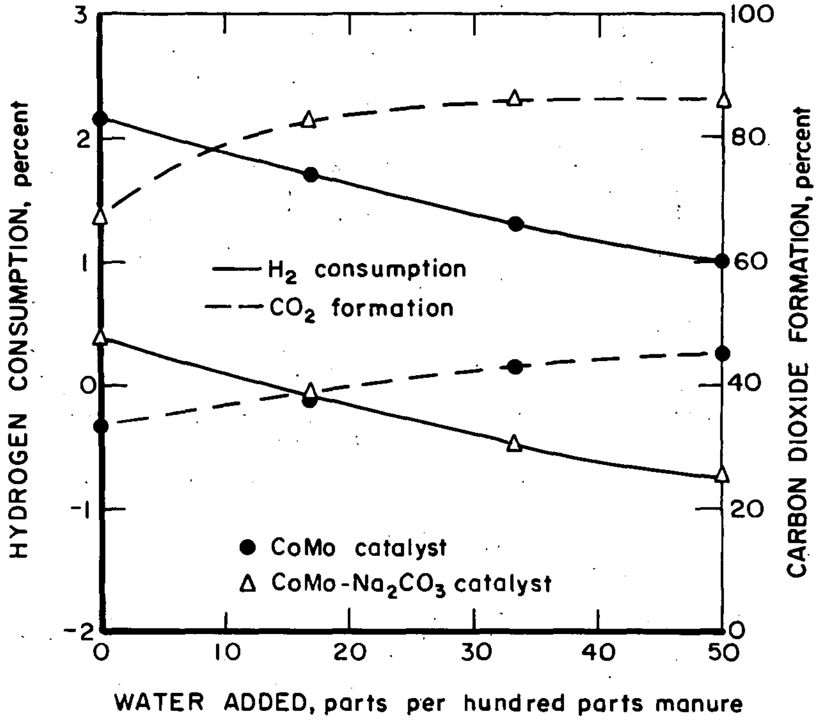

Figure 3—Effect of moisture content of manure at 380° C.

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